Colloid Group

UNIVERSITY of BRISTOL

Microgels for Controlled Uptake and Release

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McBain Medal Symposium **December 2010**

James W. McBain

1882-1953

McBain was appointed to a Bristol lectureship 1906 at 24

The first surface / colloid chemist at Bristol.

Main areas of interest: soap solutions, adsorption at interfaces.

First Leverhulme Chair 1919

Went to US (Stanford) 1927

The other person we are honouring at this meeting…!

BV Group fishing trip, Cornwall, Summer 2000

Alex and I worked together on using microgel particles as model colloidal systems for studying aggregation processes:

Salt-Induced Homoaggregation of Poly(N-isopropylacrylamide) Microgels.
A. F. Routh & B. Vincent
***Langmuir* 2002 18 5366-5369**

Flocculation of Microgel Particles with Sodium Chloride and Sodium Polystyrene Sulfonate as a Function of Temperature.
M. Rasmusson, A.F. Routh & B. Vincent
***Langmuir*, 2004 20 3536-3542**

Some Anomalous Effects of Sodium Ions on the Electrophoretic Mobility and Hetereoaggregation of Microgel Particles.
A. F. Routh & B. Vincent
***Journal of Colloid and Interface Science*, 2004 273 435-441**

Today, I want to address a different aspect of microgels:

Microgels for Controlled Uptake and Release

Two different systems will be discussed here:

(1) Anionic microgels: uptake and release (using a pH switch as the trigger) of cationic, surfactant-like dye molecules.

(2) Cationic microgels: using light as the trigger for release, with

photo-sensitive anionic surfactants

Application to anionic gold nanoparticles

acknowledgements

coworkers

- *postdocs / visitors*
- Dr Martin Snowden
- Prof Arturo Leon
- Dr Brian Saunders
- Dr Sylvie Neyret
- Dr Gayle Morris
- Dr Antonio Fernandez-Barbero
- Dr Mikael Rasmusson
- Dr Alex Routh
- Dr Melanie Bradley
- Dr Philip Karlsson

- *PhD students*
- Nick Marston
- Mike Goller
- Helen Crowther
- Andrew Loxley
- Alberto de las Nieves
- Verawan Nerapusri
- Paul Davies
- Kaizhong Fan

sponsors

- EPSRC
- EU
- Swedish Science Foundation
- British Council
- Spanish Government

- BP
- Zeneca
- Unilever
- ICI / AkzoNobel
- Paint Research Association
- Lubrizol
- GSK

SYSTEM 1

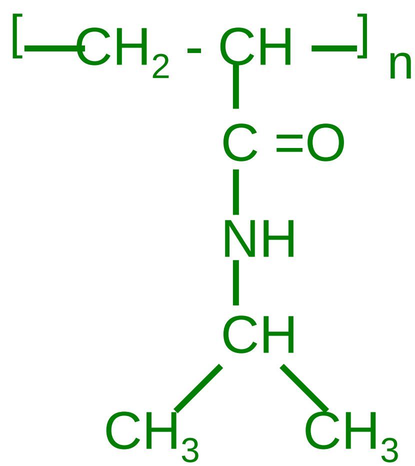
anionic microgels:

uptake of surfactant-like dye molecules
(hydrophobically modified organic salts)

Kaizhong Fan, Melanie Bradley, BV & Charl Faul. Langmuir, 2010, submitted

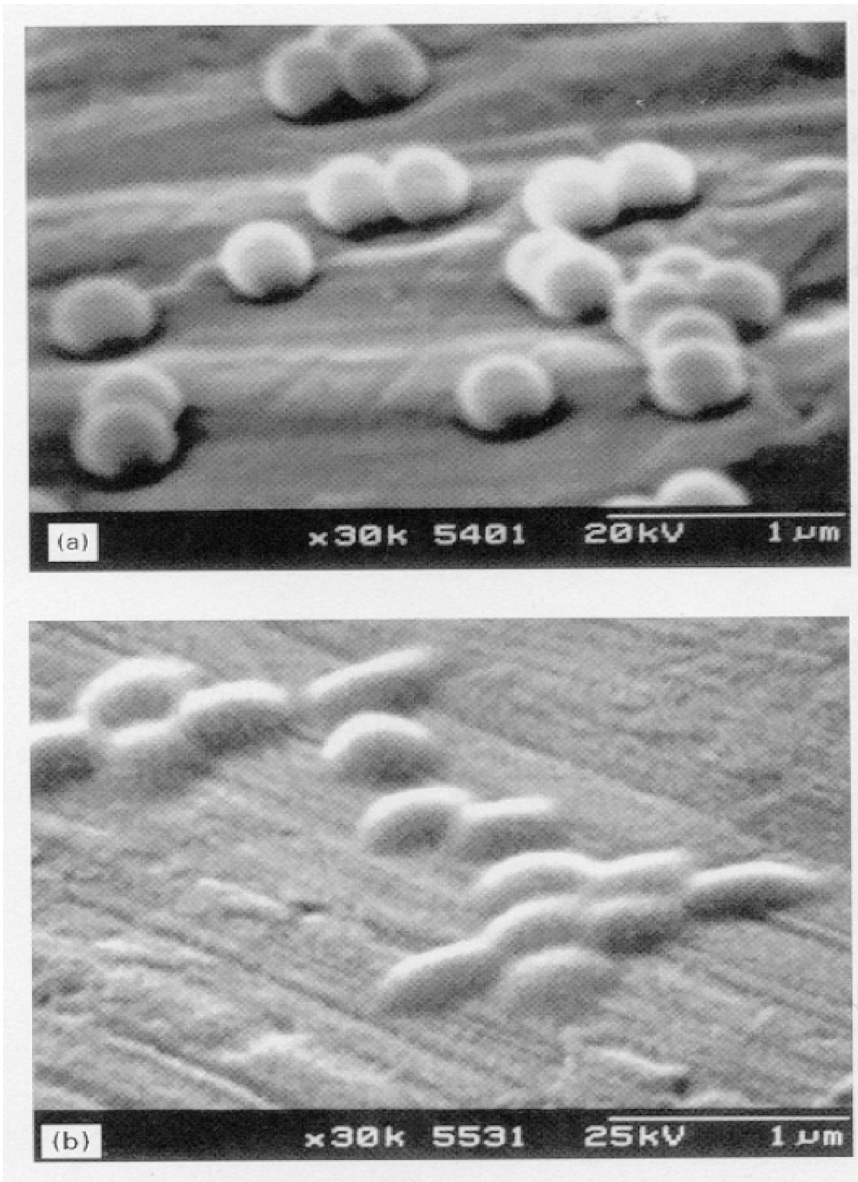
Poly (N-isopropylacrylamide)
(polyNIPAM)

Microgel Particles



Show a strong response to temperature changes; LCST at 32 °C

SEM of polyNIPAM particles



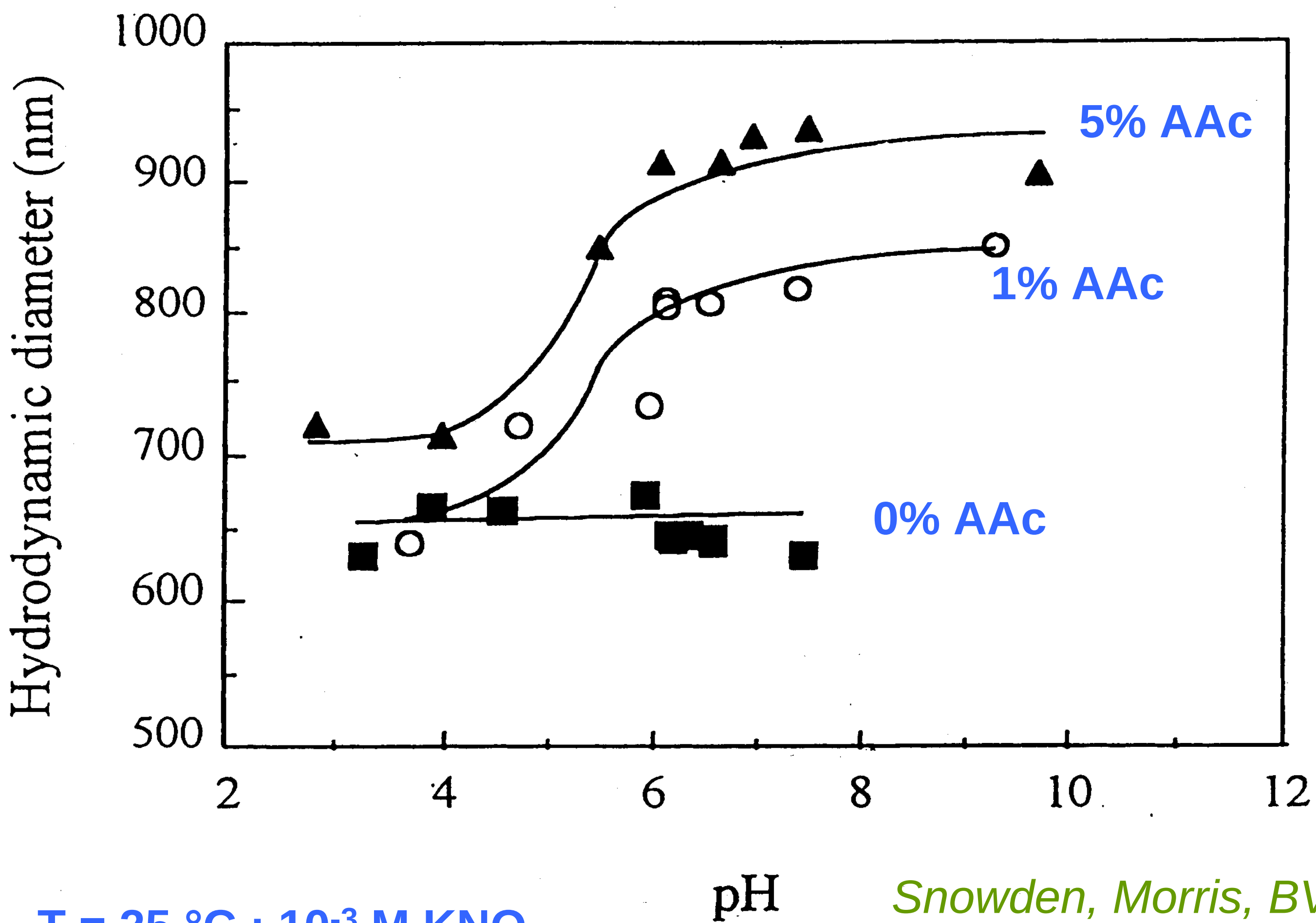
60 °C

25 °C

Saunders & BV, Colloid Polymer Sci., 1997 ***275*** *9*

pH Response ?

poly (NIPAM-co-acrylic acid) microgel particles

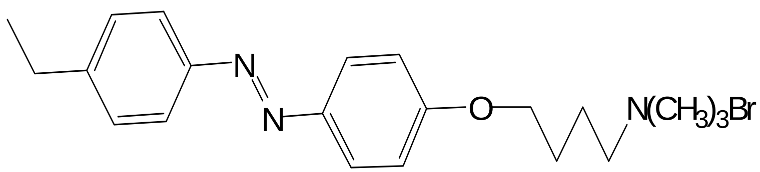


T = 25 °C ; 10^{-3} M KNO_3

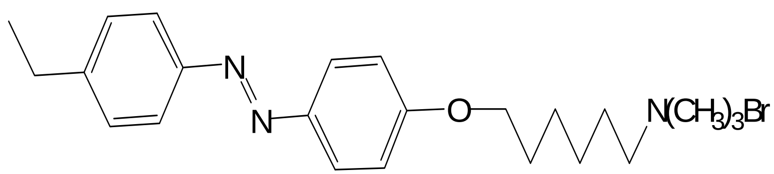
Snowden, Morris, BV J Chem. Soc Farad Trans 1996 ***92*** *5013*

Four new dye molecules have been synthesised by us:

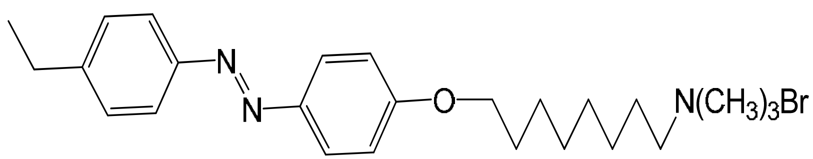
Hydrophobically [C_n]-modified, diphenylazo - based organic salts



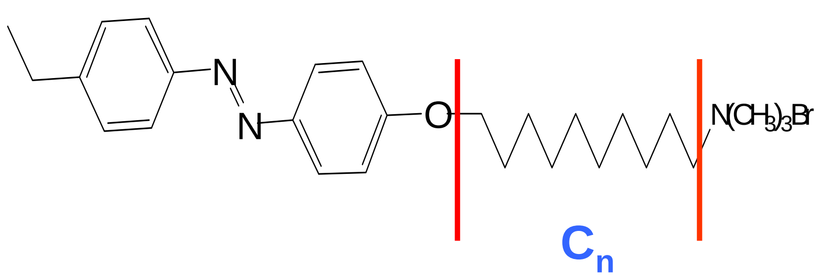
C_4OS



C_6OS

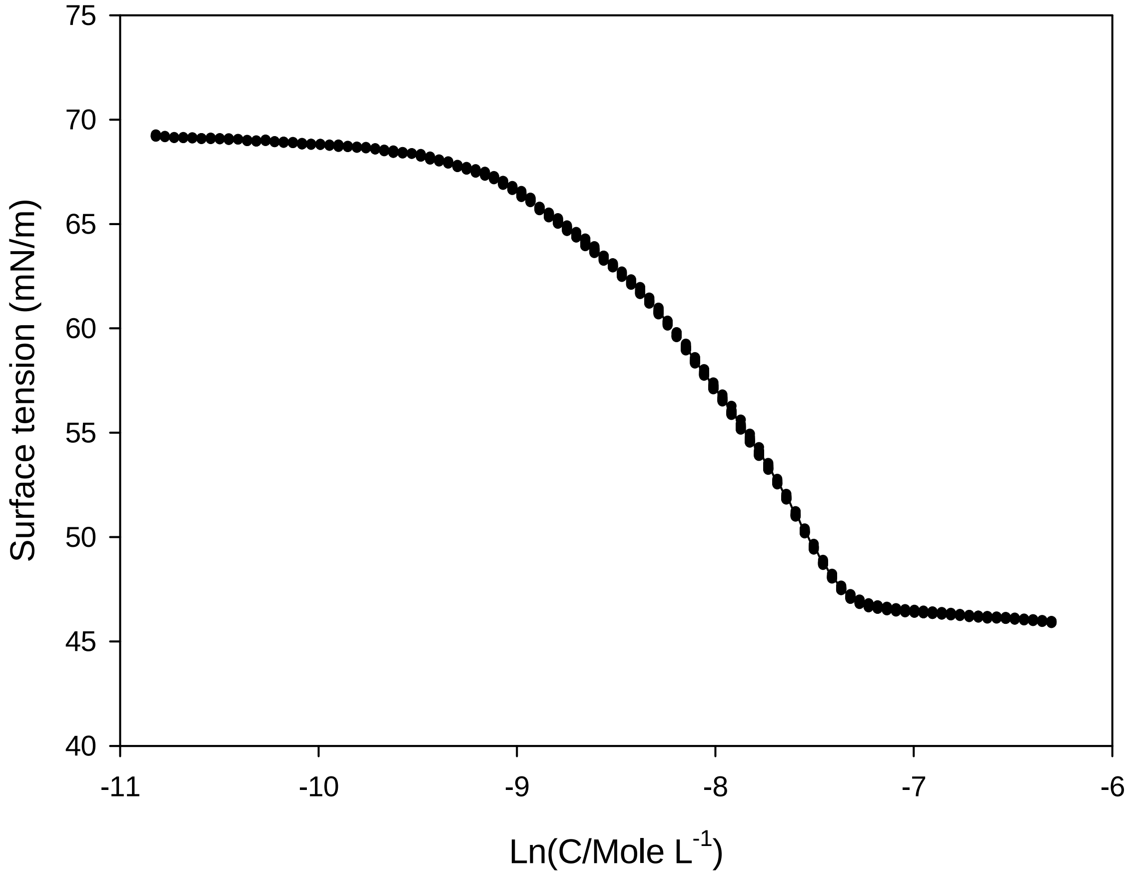


C_8OS



$C_{10}OS$

Surface tension (γ) against ln (c / M) for surfactant C8-OS at 20 °C

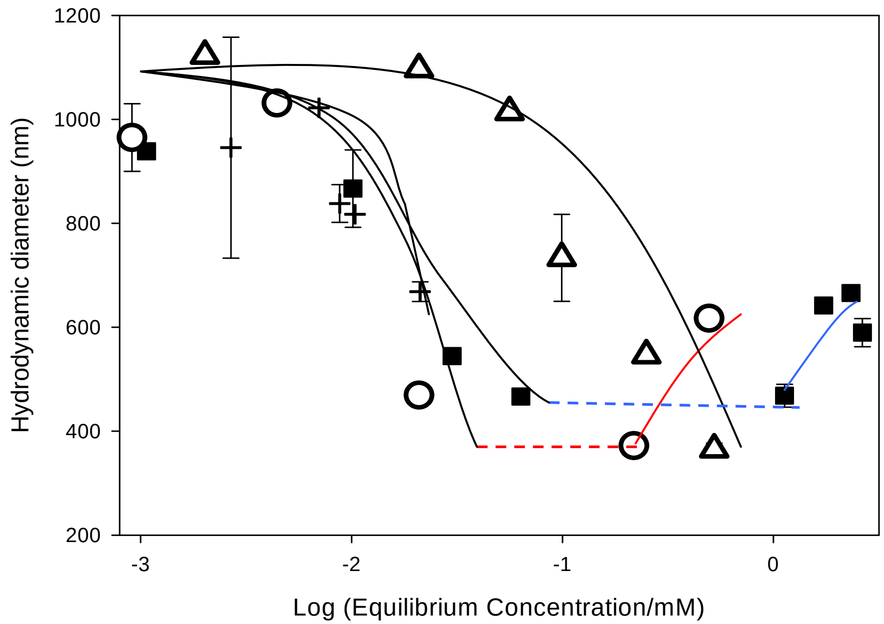


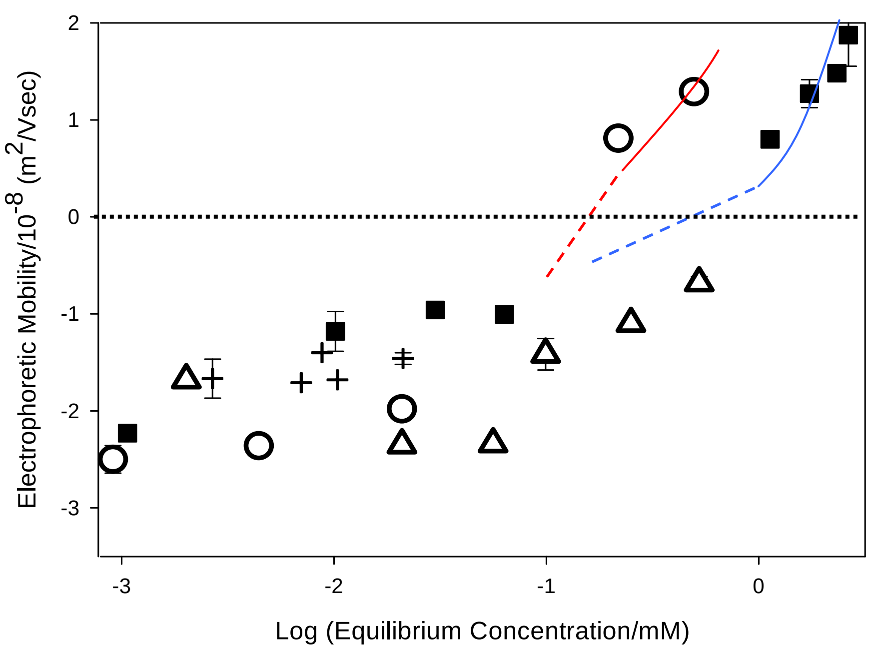
Molecular Properties

20°C

OS	M (theor.) *without* Br^- g mol^{-1}	M (exper.) from MS g mol^{-1}	c.m.c. mM	a_S nm^2	S mM
C4-OS	340	340	2.4	0.65	114
C6-OS	368	368	1.3	0.71	56
C8-OS	396	396	0.66	1.3	19
C10-OS	424	424	0.07	2.8	1.8

hydrodynamic diameter & electrophoretic mobility of the microgel particles + C_nOS





△ C_4OS ■ C_6OS

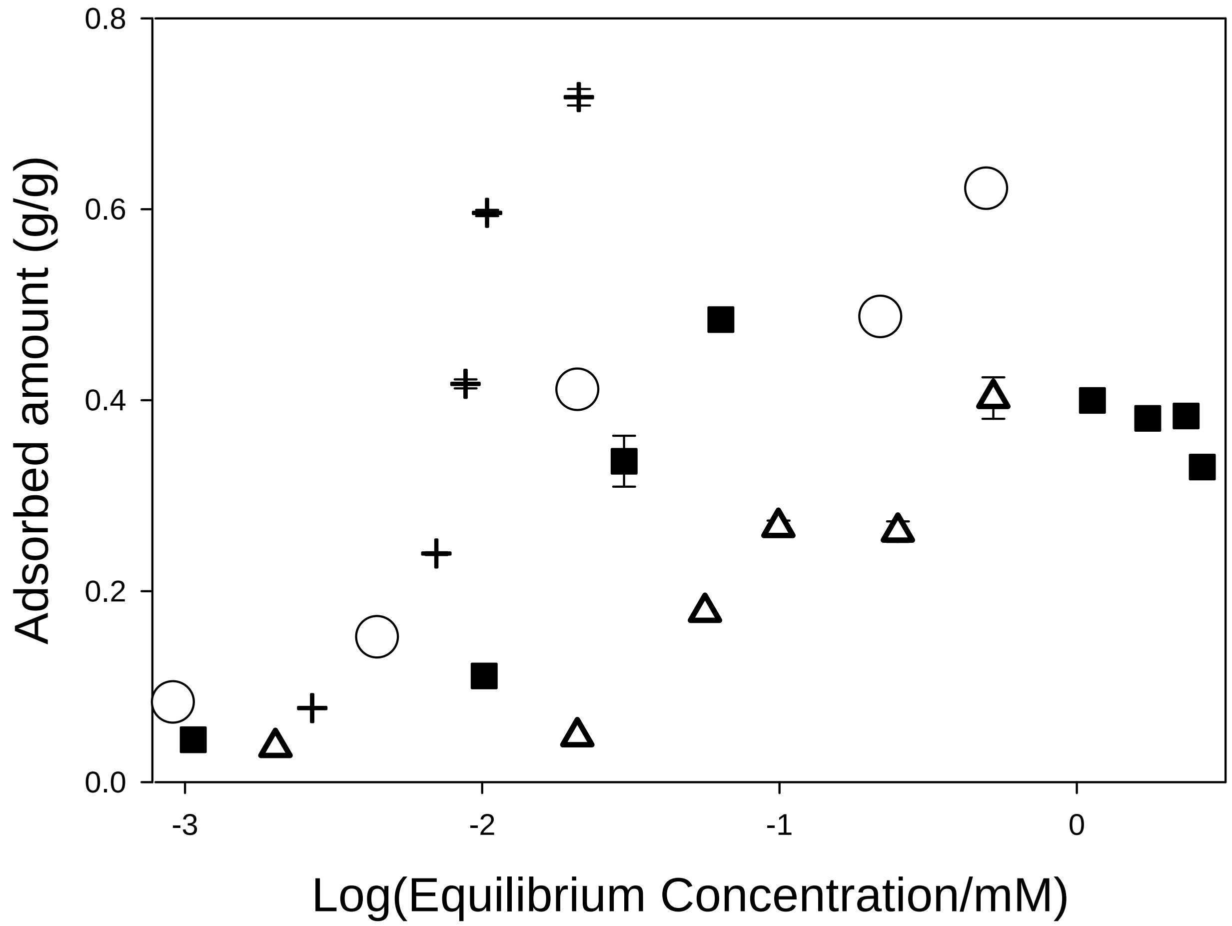
○ C_8OS + $C_{10}OS$

flocculation region

charge–reversal region

Adsorbed amounts as a function of equilibrium concentration at pH 8 and 20 °C

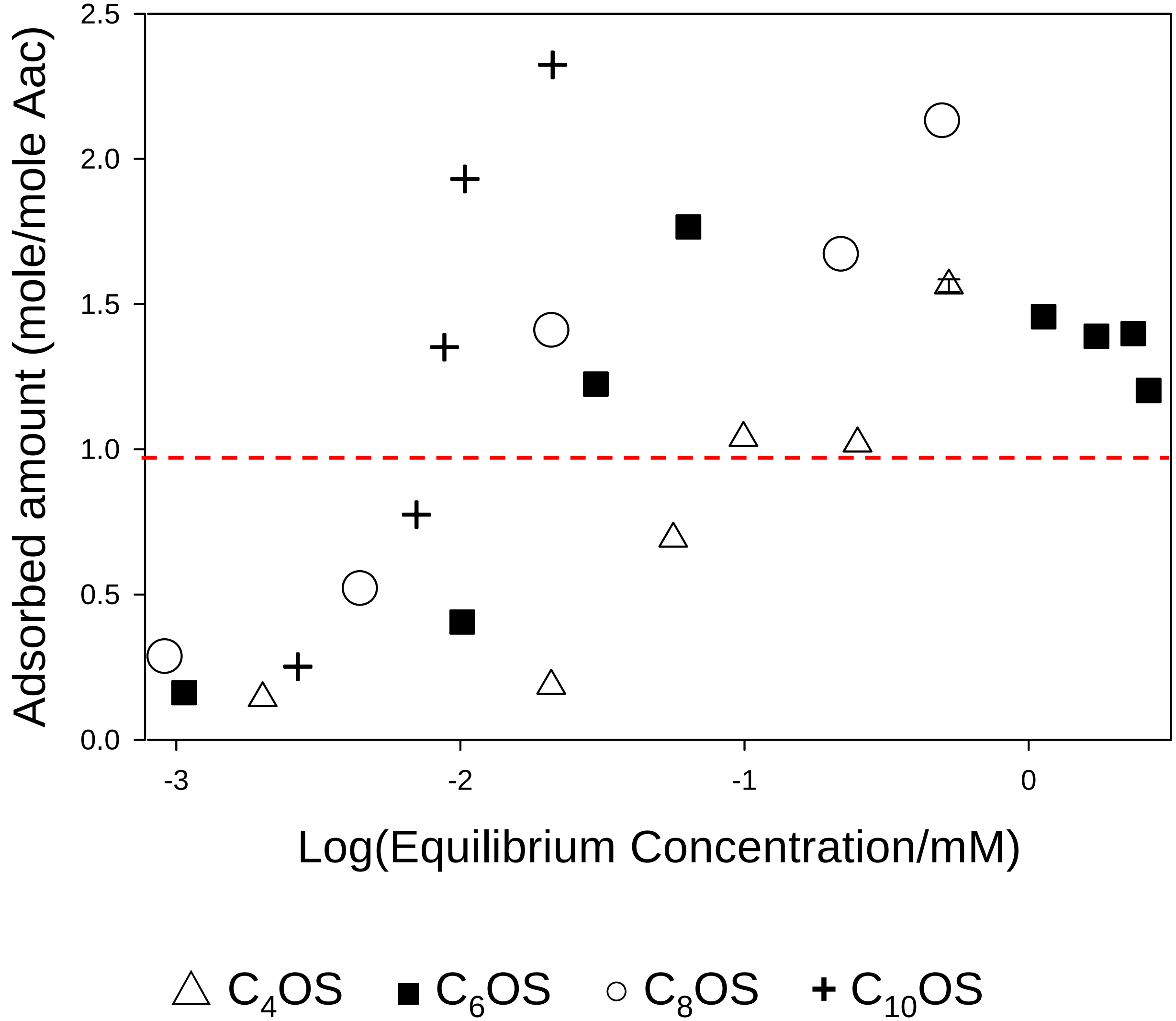
wt / wt



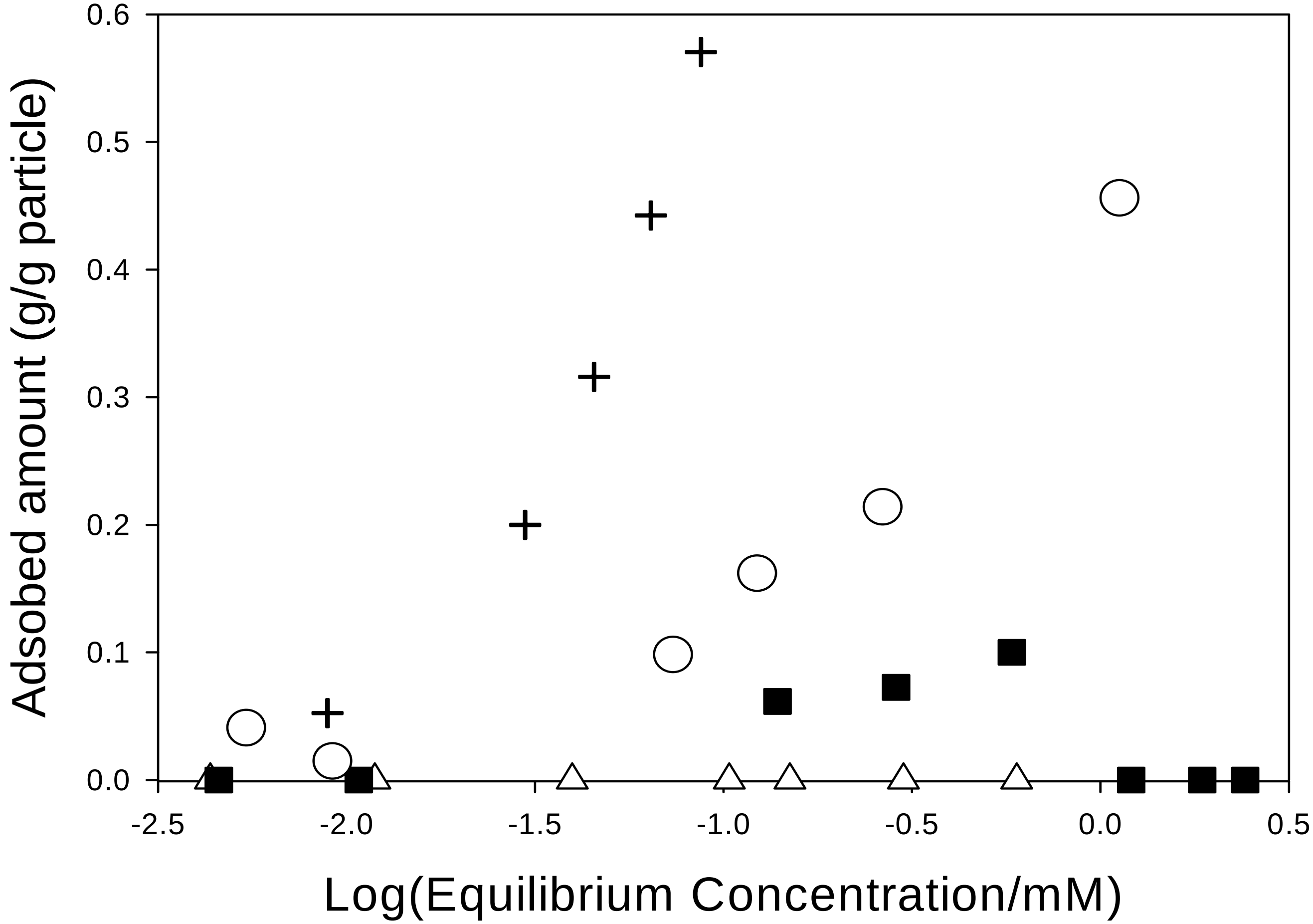
△ C_4OS ■ C_6OS ○ C_8OS + $C_{10}OS$

Adsorbed amounts as a function of equilibrium concentration at pH 8 and 20 °C

mol of OS cations/ mol of anion sites in the microgel



Adsorbed amounts as a function of equilibrium concentration
Switch pH from 8 to 2.5 (i.e. switch-off electrostatic attraction)

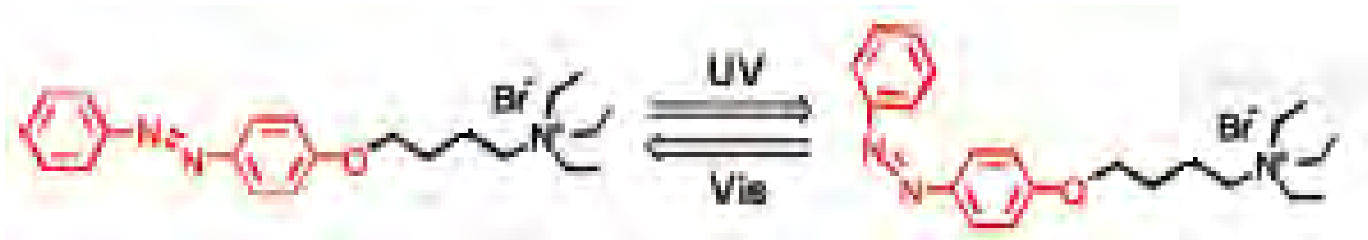


△ C_4OS ■ C_6OS ○ C_8OS + $C_{10}OS$

picture of freeze-dried microgel particles + absorbed C_8-OS:

Conformational Response to U.V. irradiation:

trans to cis rearrangement



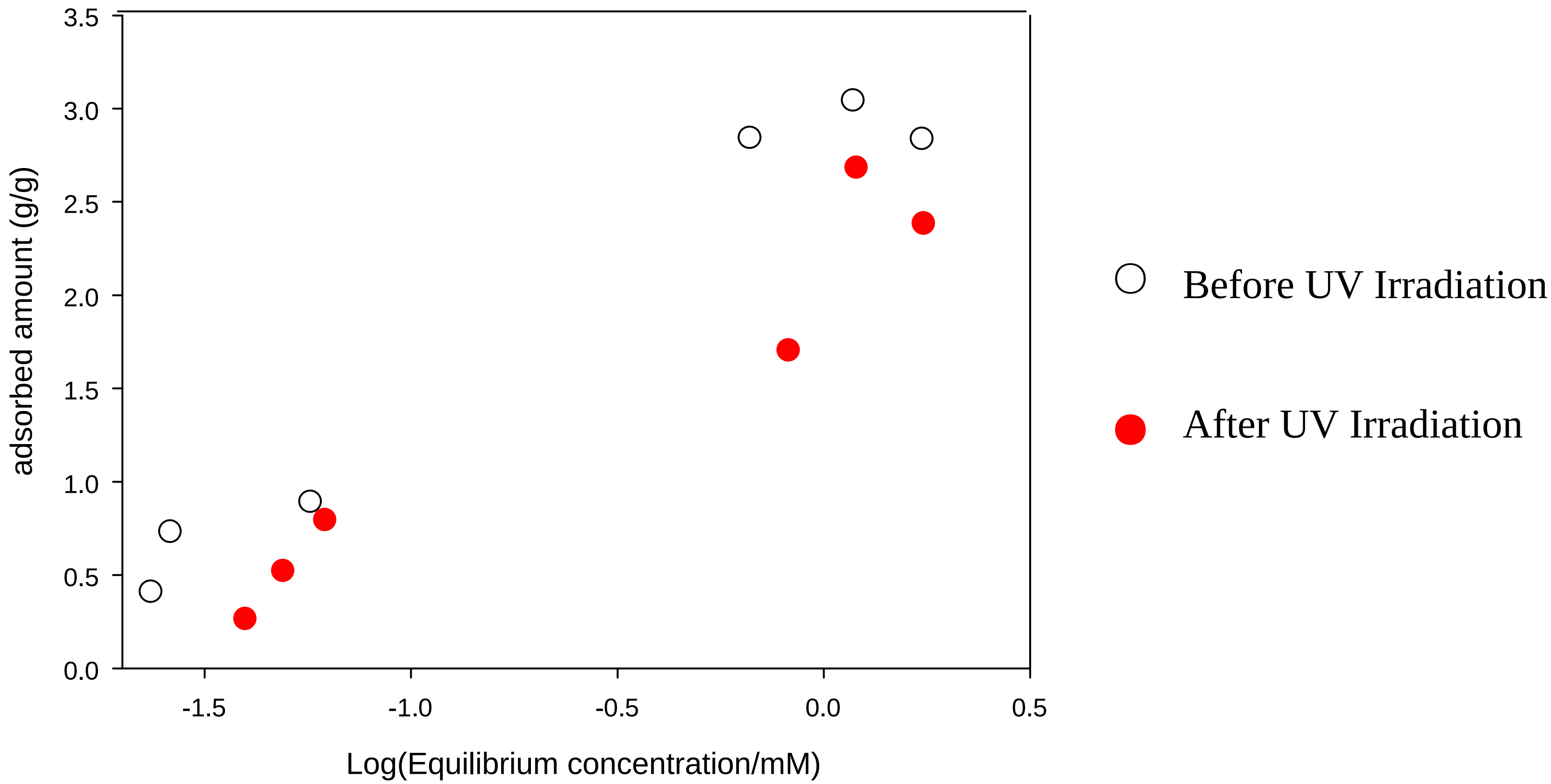
CMC= 4.6 mM

CMC= 10.5 mM

Chain “packing” efficiency decreased ?

T. Hayashita, T. Kurosawa, T. Miyata, K. Tanaka, and M. Igawa. Colloid Polymer Sci., 1994 272 1611

Effect of uv radiation of absorption of C_6OS into anionic microgels:



Might be able to pursue this concept to develop the use of uv light as a trigger mechanism for release?

However, there is an alternative approach:

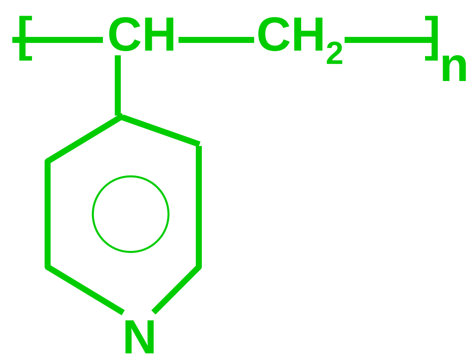
SYSTEM 2

cationic microgels + light-degradable anionic surfactants

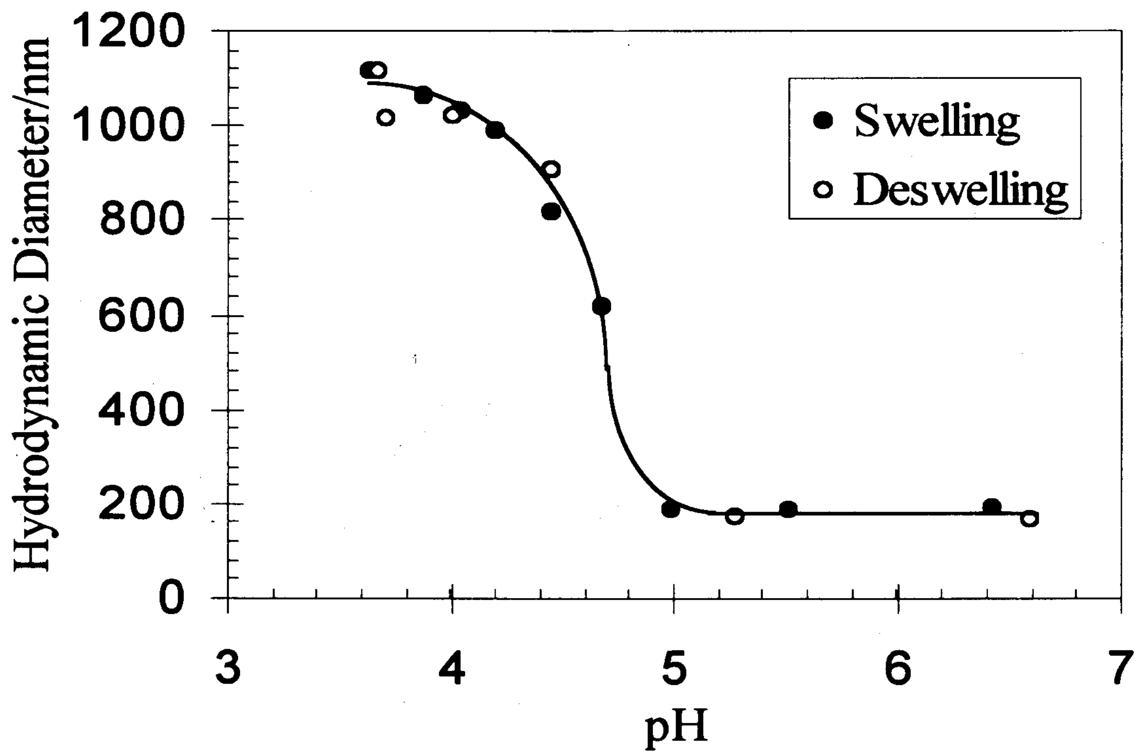
to give a light-induced triggered release mechanism.

Application to anionic gold nanoparticles

Poly(vinylpyridine) [PVP] Microgel Particles



reversibility of swelling with pH



99.5% 2-Vinylpyridine
0.5% DVB

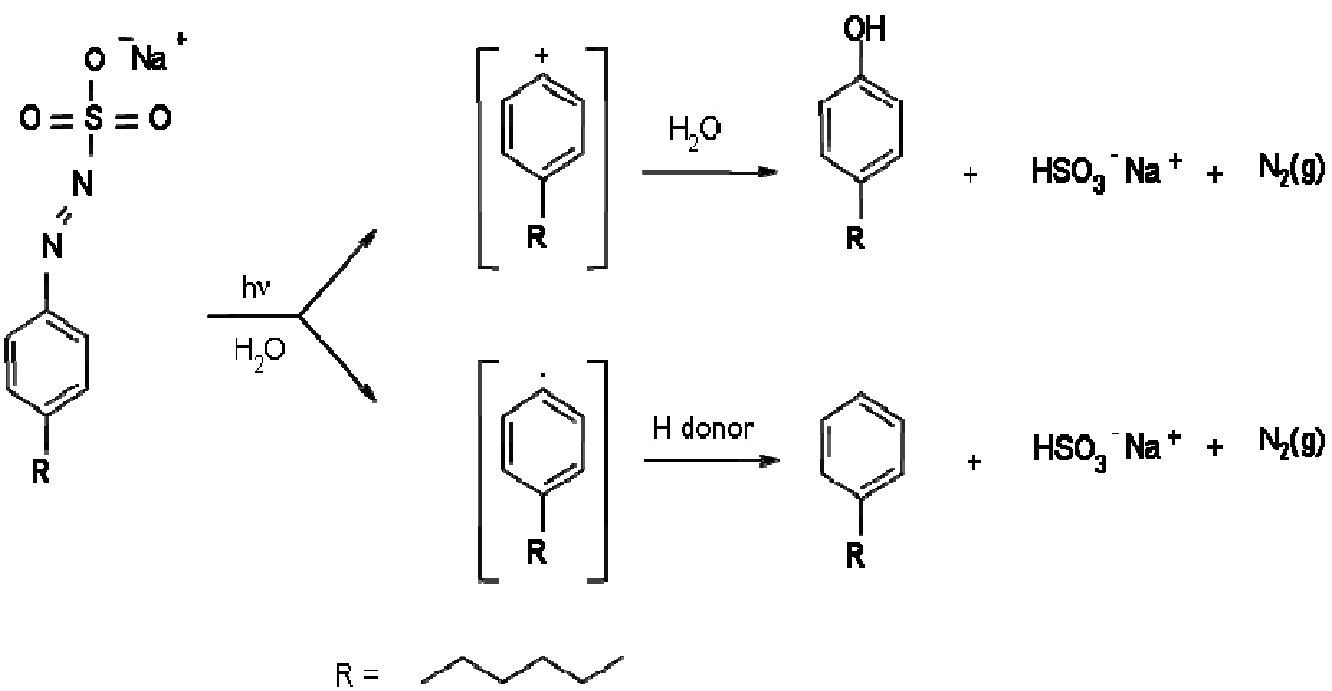
Loxley & BV

Colloid Polymer Sci.

1997 ***275*** *1108*

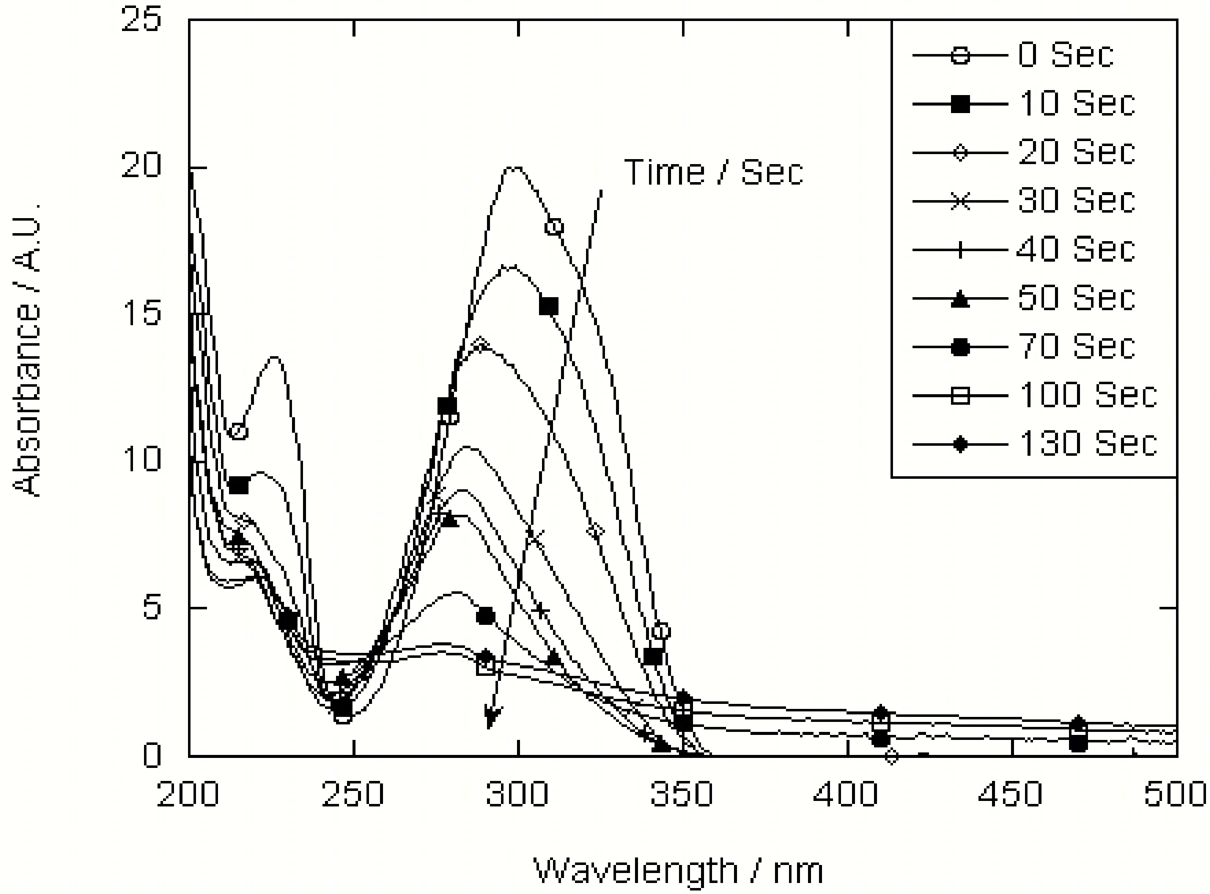
Light–degradable anionic surfactants

Photo-dissociation of 4-hexylphenylazosulfonate (C_6PAS) :

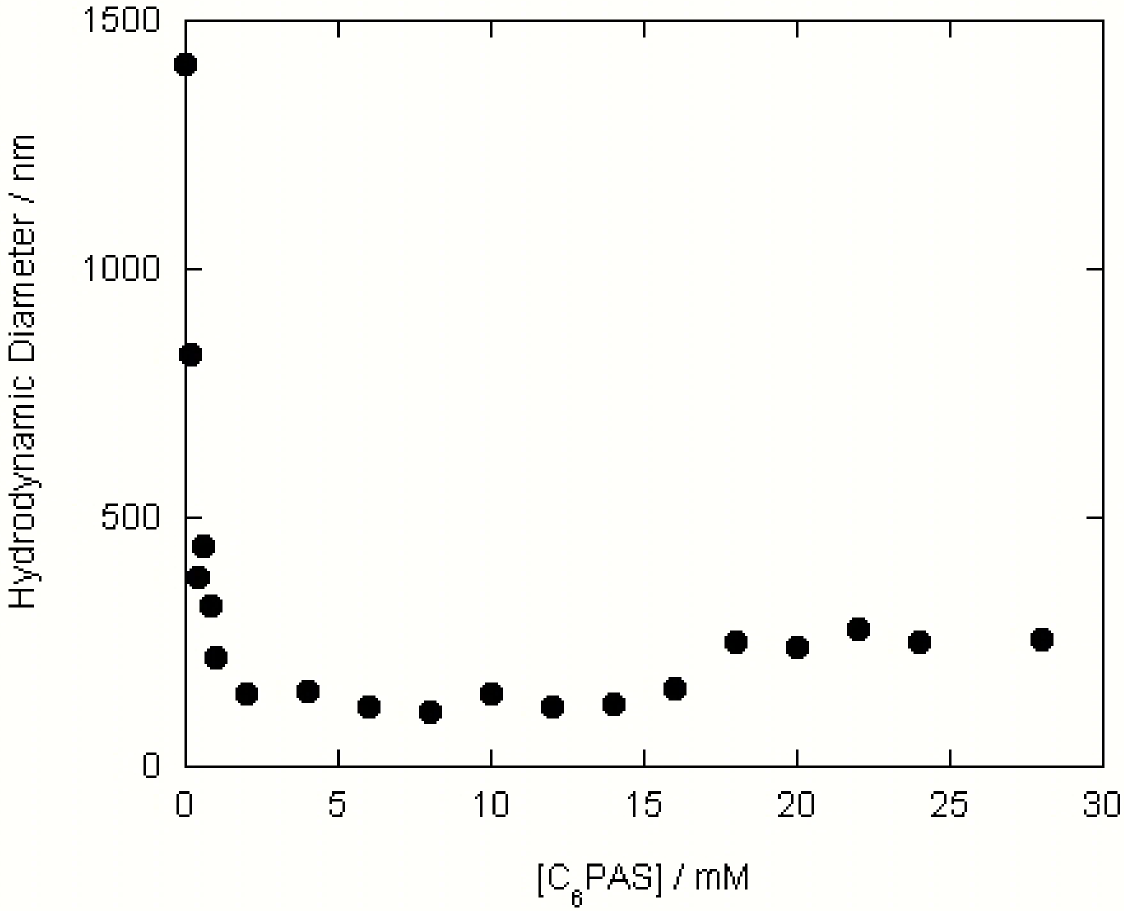


Bradley, BV, Eastoe et al., Langmuir 2006 ***22*** *101*

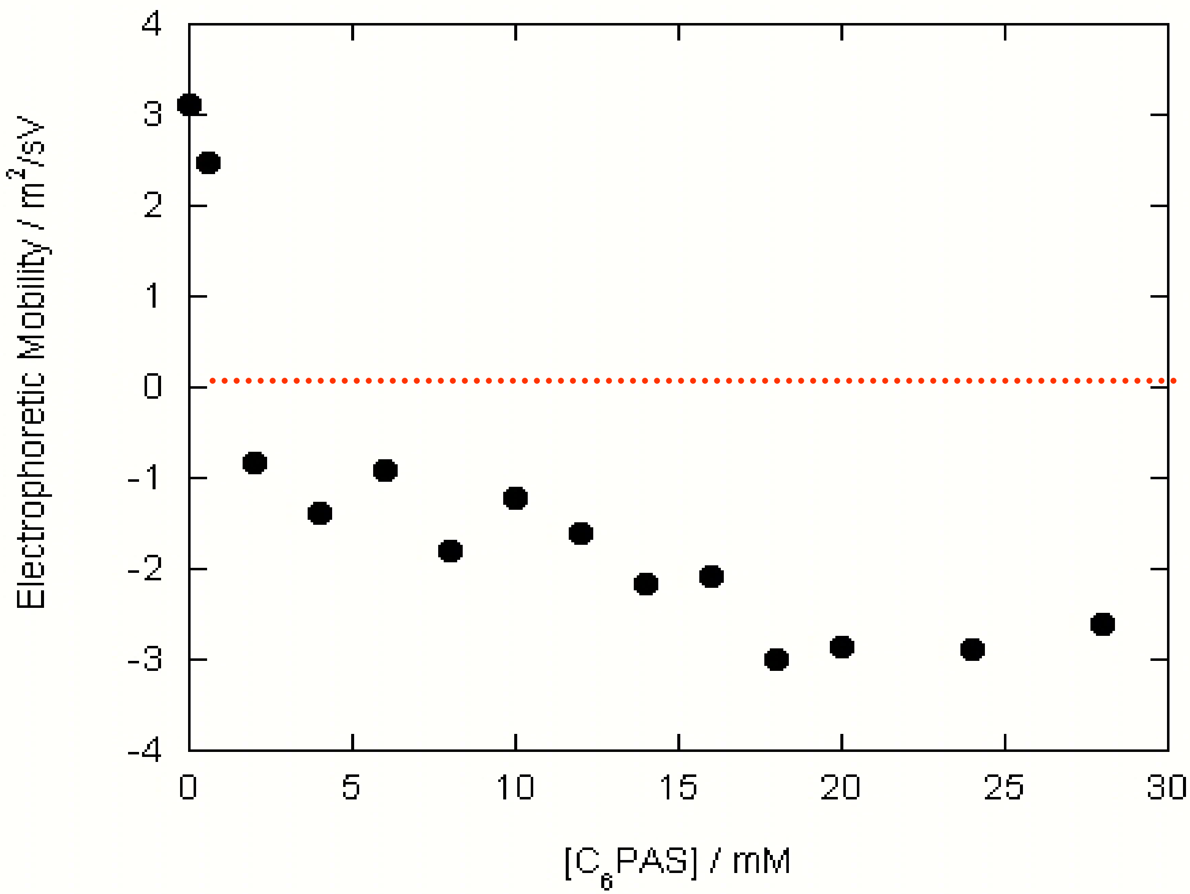
Absorbance Spectrum of 2mM C_6PAS Solution with time



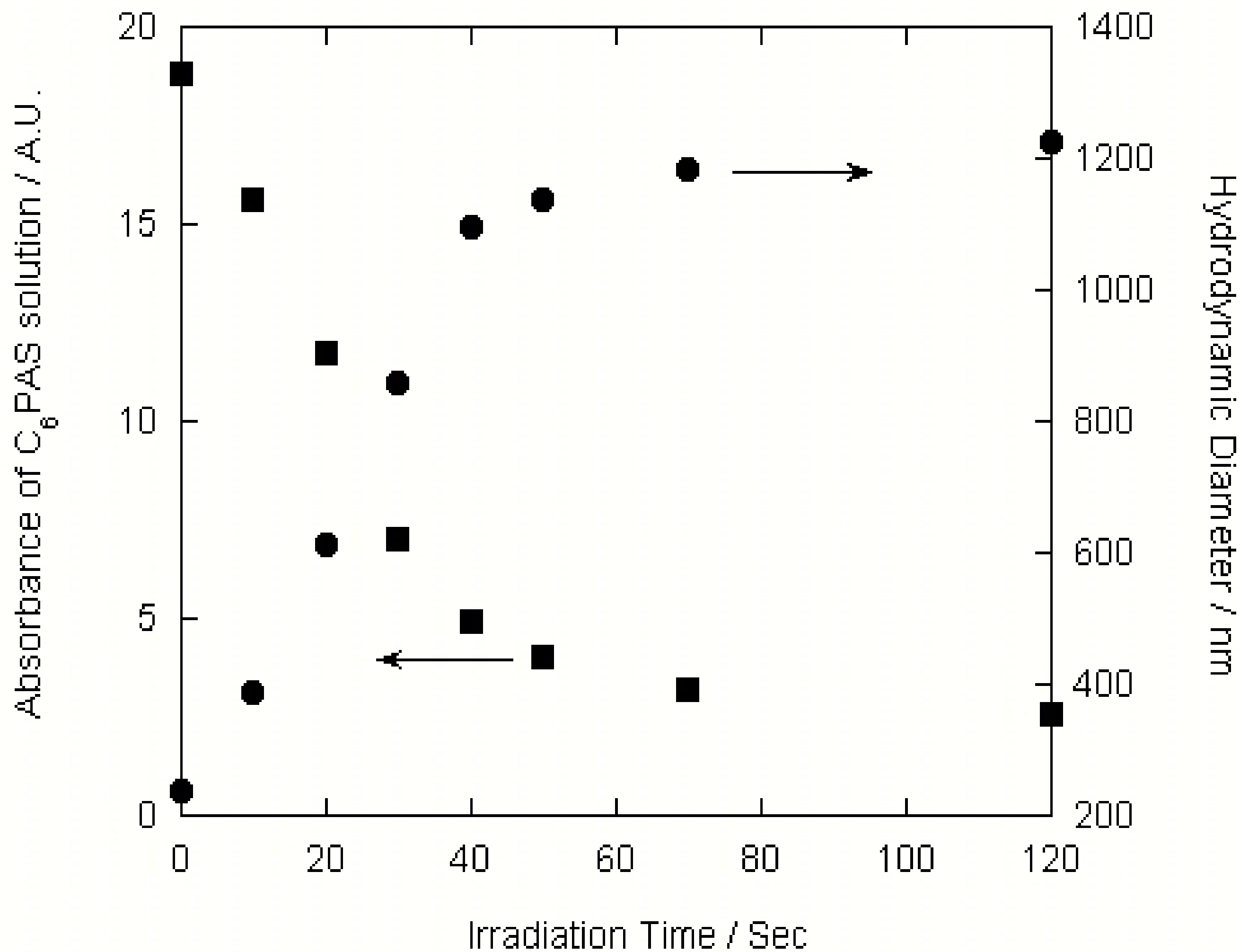
Absorption of C_6PAS by PVP Microgel Particles



Electrophoretic Mobility



Irradiation of PVP + C_6PAS (2mM) System

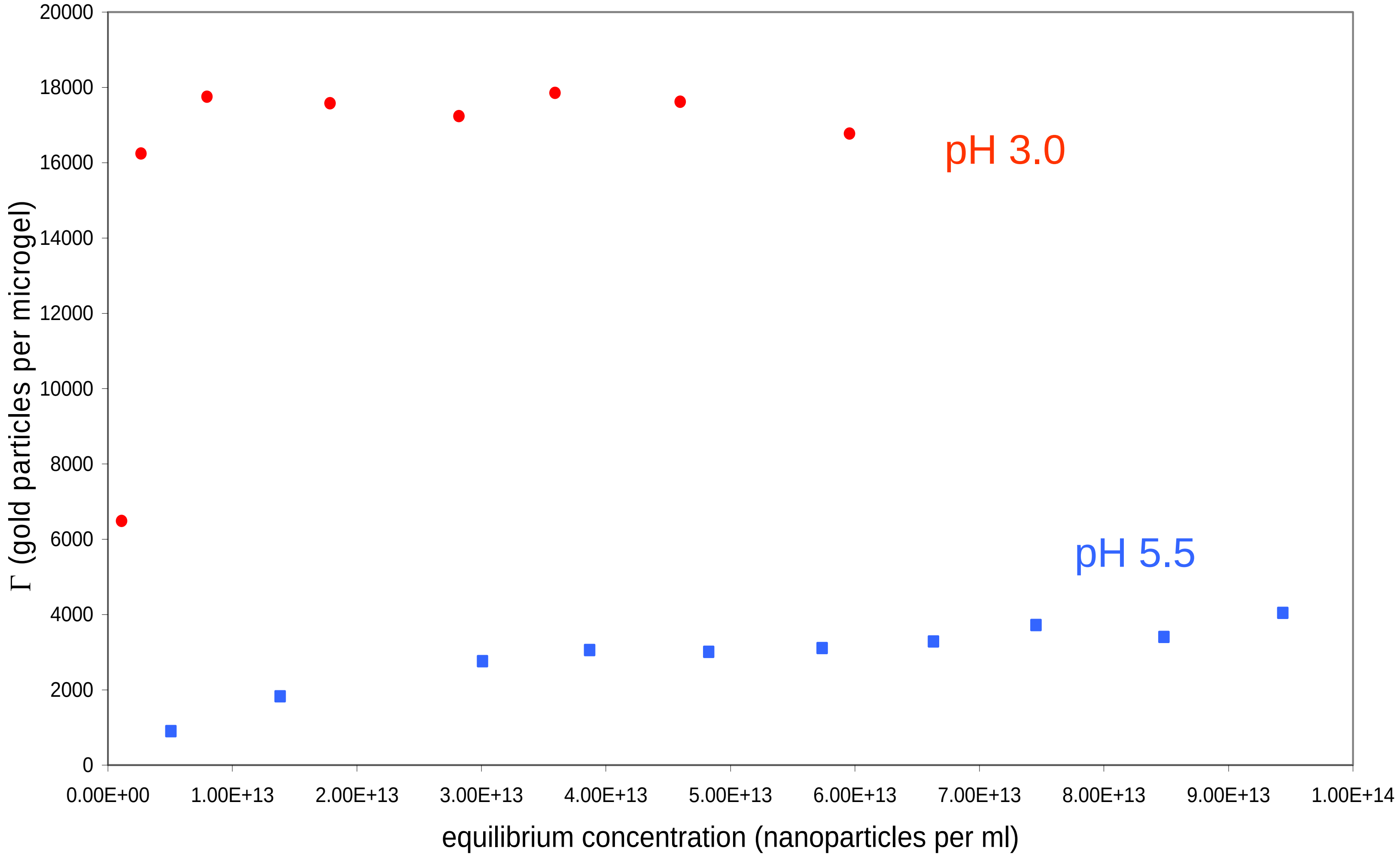


Absorption of Gold Nanoparticles

Into PVP Microgel Particles

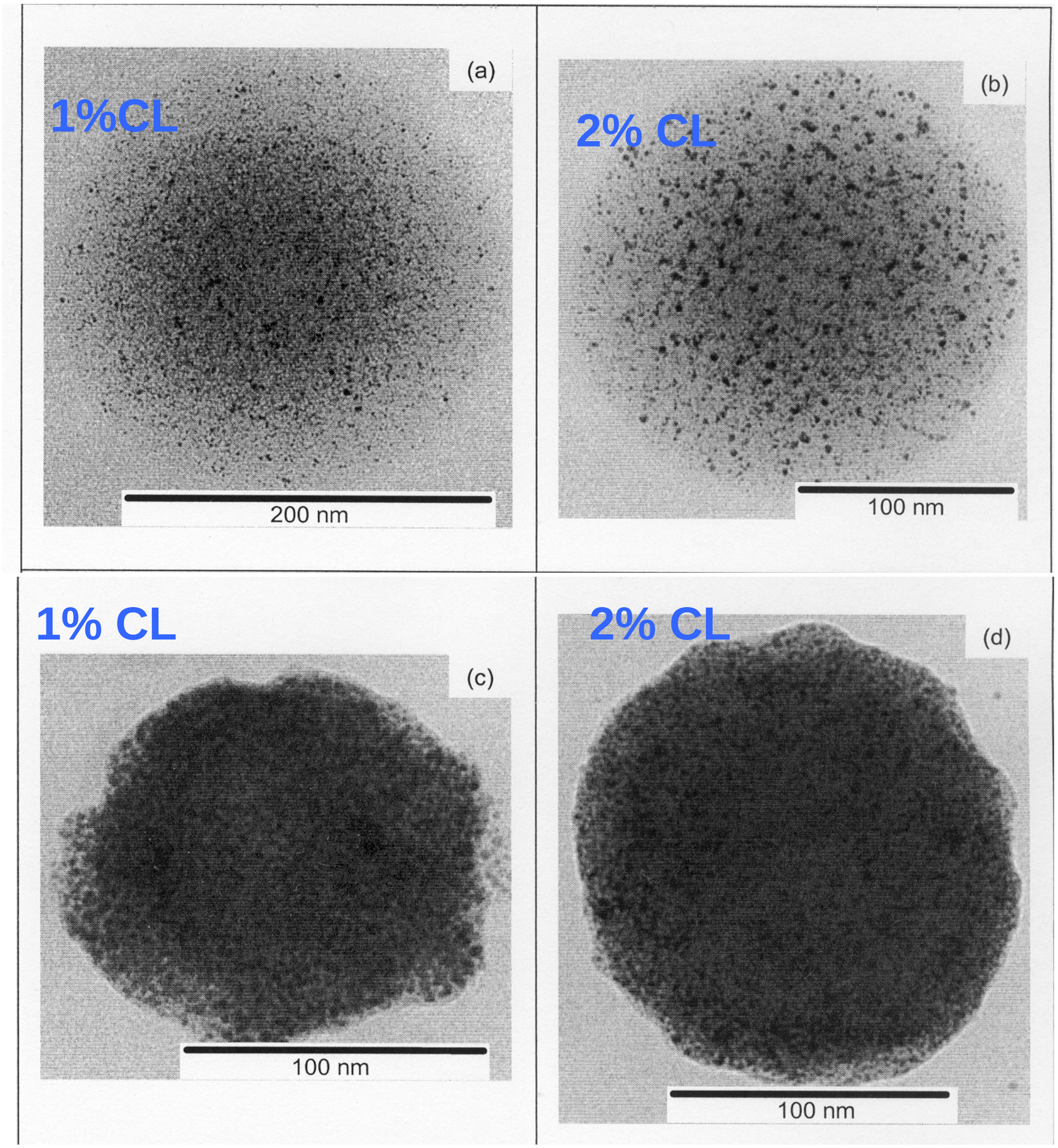
P.T.Davies & B.V., Colloids & Surfaces A, 2010 354 99

Absorption of Gold Nanoparticles into PVP Microgel Particles



Au particles 2-3 nm

TEM



pH 6

pH 3

Current work (+ Mel Bradley)

Preliminary Results

(1) Absorb a mixture anionic C_6PAS and anionic gold particles into *amphoteric* microgel particles at low pH (i.e. initially positively charged). The microgel particles collapse, trapping the Au nanoparticles.

(2) Apply light and a pH switch (to a higher value) to effect microgel swelling and release of the Au particles. Seems to work! Need to make results more quantitative.

(3) This concept could be extended to other nanoparticles or large molecules for targeted delivery (e.g. drugs - would need biocompatible systems!)

CONCLUSIONS

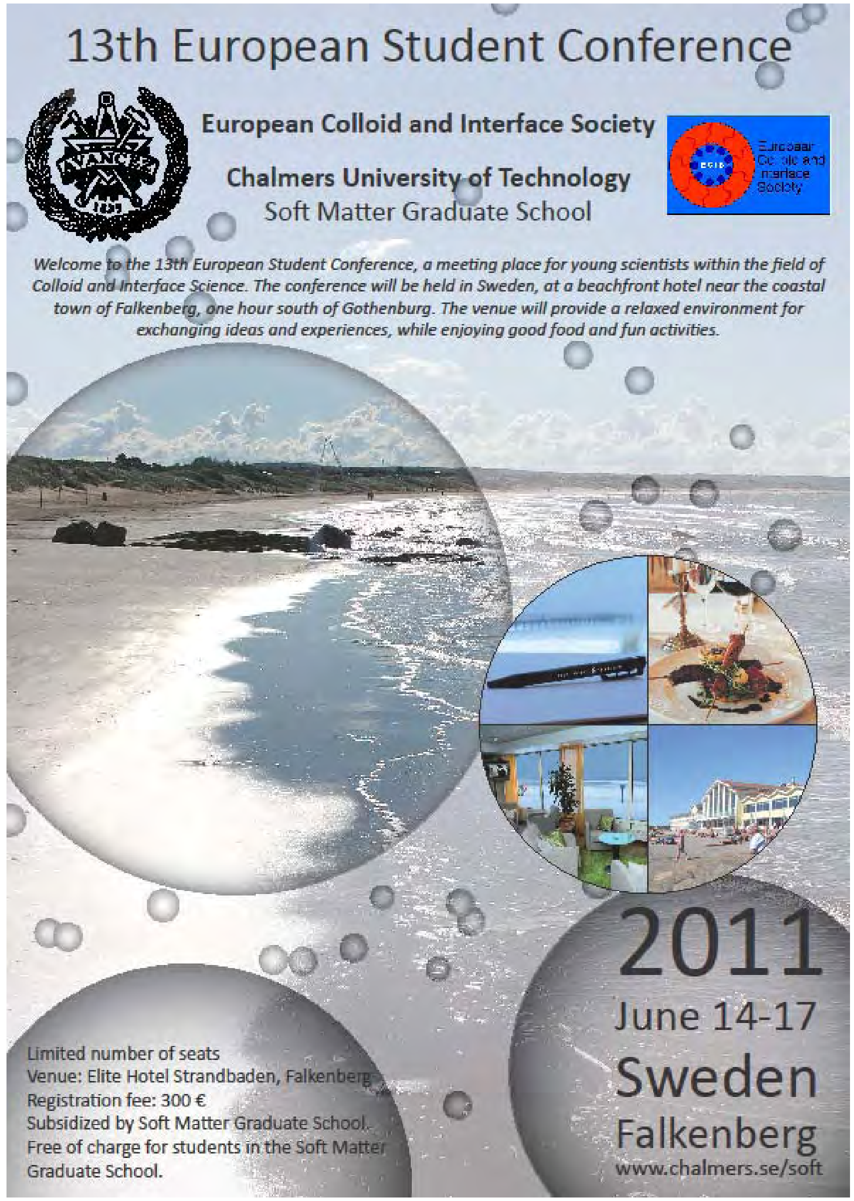
- Microgel particles can be used to (selectively) absorb a variety of species: e.g. organic molecules, ions, surfactants, polymers, polyelectrolytes and biopolymers, nanoparticles.

- Selectivity can be achieved by: (i) control of mesh-size (cross-link density); (ii) specific interactions.

- Release can be achieved by a suitable switch in e.g. temperature, solvent composition or pH, or the use of light.

- Not discussed here but: monolayers of microgel particles can be created on suitable substrates; these may also be used for controlled / selective uptake and release.

One last thing!



e-mail contact: markus.andersson@chalmers.se

Thank you for listening!